

catena-Poly[[diaquanickel(II)]-bis(μ -2- {[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]- sulfanyl}acetato])

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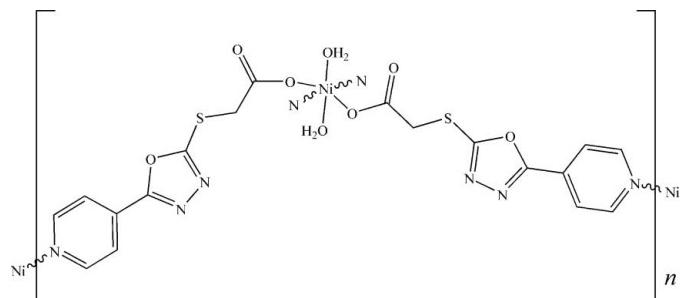
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Key indicators: single-crystal X-ray study; $T = 293\text{ K}$; mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$; R factor = 0.028; wR factor = 0.068; data-to-parameter ratio = 11.0.

In the title compound, $[\text{Ni}(\text{C}_9\text{H}_6\text{N}_3\text{O}_3\text{S})_2(\text{H}_2\text{O})_2]_n$, the Ni^{II} atom, located on an inversion center, is ligated in an octahedral geometry by two carboxylate O atoms from two 2-[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]sulfanylacetate (L) ligands and two O atoms from water molecules in the equatorial plane, and two pyridine N atoms from other two L ligands at the apical sites. Two L ligands bridge pairs of metal atoms in an antiparallel manner, forming centrosymmetric dinuclear quasi-rectangular units which are linked into infinite double-stranded chains parallel to [100]. O—H \cdots O hydrogen bonds between the coordinating water molecules and the carboxylate groups of the L ligand as well as interchain S \cdots N interactions [2.726 (2)–3.363 (2) \AA] lead to the formation of a layer structure parallel to (001).

Related literature

For coordination polymers of 1,3,4-oxadiazole-2-thione, see: Wu *et al.* (2010); Lundin *et al.* (2006); Wang *et al.* (2007). For coordination polymers of symmetric pyridyl-containing oxadiazole ligands, see: Ma *et al.* (2007); Du *et al.* (2006). For unsymmetric pyridyl-containing oxadiazole ligands, see: Wang & Li (2011).



Experimental

Crystal data

$[\text{Ni}(\text{C}_9\text{H}_6\text{N}_3\text{O}_3\text{S})_2(\text{H}_2\text{O})_2]$	$V = 1034.5 (3)\text{ \AA}^3$
$M_r = 567.20$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.8862 (18)\text{ \AA}$	$\mu = 1.20\text{ mm}^{-1}$
$b = 5.6431 (9)\text{ \AA}$	$T = 293\text{ K}$
$c = 15.500 (2)\text{ \AA}$	$0.15 \times 0.13 \times 0.07\text{ mm}$
$\beta = 95.687 (2)^\circ$	

Data collection

Siemens SMART CCD diffractometer	1822 independent reflections
7195 measured reflections	1488 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.068$	$\Delta\rho_{\text{max}} = 0.25\text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.28\text{ e \AA}^{-3}$
1822 reflections	
166 parameters	
2 restraints	

Table 1
Selected bond lengths (\AA).

Ni1—O2	2.0702 (16)	Ni1—N1^i	2.1157 (19)
Ni1—O4	2.0781 (18)		

Symmetry code: (i) $x + 1, y, z$.

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$\text{O4—H4A} \cdots \text{O3}$	0.82 (1)	1.83 (1)	2.633 (3)	167 (3)
$\text{O4—H4B} \cdots \text{O2}^{\text{ii}}$	0.82 (1)	2.11 (2)	2.857 (3)	153 (3)

Symmetry code: (ii) $x, y - 1, z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2075).

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supplementary materials

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catena-Poly[[diaquanickel(II)]-bis(μ -2-{{[5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl]sulfanyl}acetato})]

Ru-Qin Gao, Chao-Hui Xia and Guo-Ting Li

Comment

There have been considerable interests in the coordination polymers of 1,3,4-oxadiazole-2-thione because of their intriguing architectures (Wu, *et al.*, 2010) and potential applications as functional materials (Lundin, *et al.*, 2006; Wang, *et al.*, 2007). In particular, pyridyl-containing oxadiazole ligands, such as symmetric 5-phenyl-1,3,4-oxadiazole-2-thione (Ma, *et al.*, 2007) and 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Du, *et al.*, 2006), have been extensively explored in the construction of porous coordination polymers. As our continuous work in this aspect (Wang & Li, 2011), we report that the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and sodium(I) salt of 2-(5-(pyridin-4-yl)-1,3,4-oxadiazol-2-ylthio)acetic acid (HL) leads to a new complex $[\text{Ni}(L)_2(\text{H}_2\text{O})_2]_n$ (1) herein.

In (1) the Ni^{II} center is located at the inversion center ligated by two carboxylato O atoms from two deprotonated L and two O atoms from water molecules in the equatorial plane, and two pyridyl N atoms from other two deprotonated L at the apical sites. Thus the Ni^{II} ion is in a six-coordinated octahedral coordination geometry (Fig. 1). The bond distances of $\text{Ni}—\text{O}$ and $\text{Ni}—\text{N}$ range from 2.070 (2) to 2.116 (2) Å, while $\text{O}—\text{Ni}—\text{N}$ angles range from 85.90 (7) to 94.10 (7) °, indicating a slight distortion from an ideal octahedron.

Complex (1) displays an extended infinite double-strand chain structure constructed of dinuclear quasi-rectangle units (Fig. 2). The dinuclear quasi-rectangle units are centrosymmetric and formed by two L anions antiparallelly bridging two metal centers in monodentate modes with two nickel atoms and two methylene carbon atoms of the L at the corners and the diagonal $\text{Ni}…\text{Ni}$ distances of 11.886 (2) Å. As for L , the pyridyl group and the acetate group deviate from the center ring of oxadiazole-2-thione group, with the dihedral angels being 36.0 (7) and 88.5 (7) °, respectively. Notably, the conformation of L is apt to the dinuclear quasi-rectangle which is further stabilized by $\text{CH}…\pi$ stacking interactions between antiparallel the pyridyl-1,3,4-oxadiazol groups of the L in the same rectangle unit with the distances of $\text{H}_{\text{pyridyl}}$ to centroid of oxadiazol group being 3.320 (2) Å and 3.353 (2) Å. The chains of complex (1) are connected by $\text{O}—\text{H}…\text{O}$ hydrogen bonds between the coordinated water molecules (as donors) and the carboxylate groups of L (as acceptors), leading to the formation of a two-dimensional network structure (Fig. 2, Table 3). Additionally, the interchain weak interactions between S and N of the oxadiazole-2-thione groups of L stabilize the layer structure (the distances of $\text{S}…\text{N}$ being in a range of 2.726 (2) to 3.363 (2) Å).

Experimental

For the synthesis of sodium(I) salt of ligand 2-(5-(pyridin-4-yl)-1,3,4-oxadiazol-2-ylthio)acetic acid (HL), see: Wang & Li, (2011). The title compound (1). $n(\text{H}_2\text{O})$ was prepared according to the following process. A mixture of NaL (51.8 mg, 0.2 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.1 mmol) and deionized water (20 ml) was stirred for 30 minutes and then filtered. The filtrate was allowed to evaporate at room temperature for three days, and then green needle crystals were obtain in 72% yield. Selected IR (cm^{-1} , KBr pellet): 3374(*m*), 3091(*w*), 2994(*w*), 1621(*m*), 1579(*s*), 1463(*s*), 1382(*s*), 1224(*m*),

1192(*m*), 1065(*m*), 958(*w*), 707(*s*), 586(*w*).

Refinement

The H atoms of water were located from difference Fourier maps and included in the final refinement by using geometrical restraints, while the other hydrogen atom positions were generated geometrically and these H atoms were allowed to ride on their parent atoms.

Computing details

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

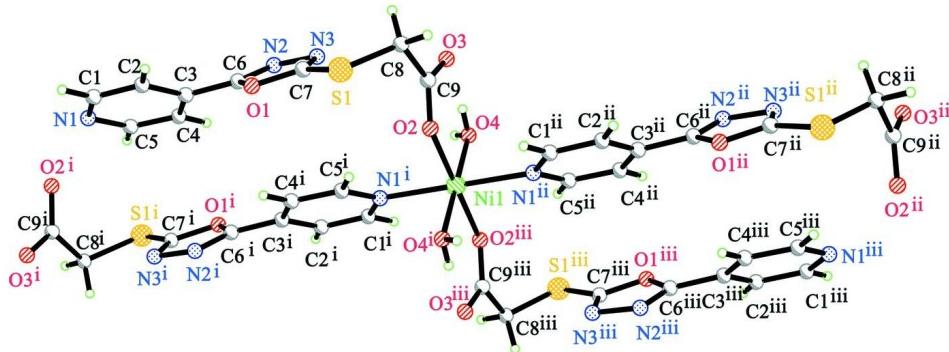


Figure 1

Coordination environment of the nickel atom in (1). Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (i) $-x + 1, -y, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y, -z + 1$.

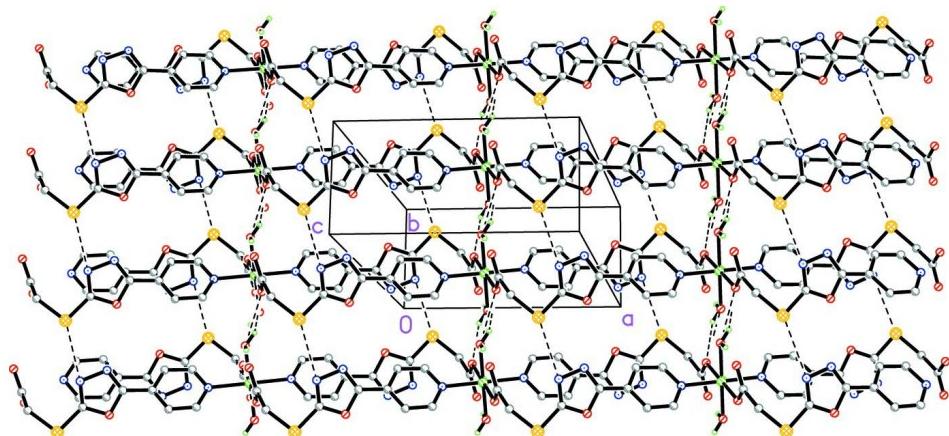


Figure 2

View of the two-dimensional network structure in (1) formed by interchain S···N interactions and multiple O—H···O hydrogen-bonding interactions

catena-Poly[[diaquanickel(II)]-bis(μ -2-{{5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl}sulfanyl}acetato)]*Crystal data*

$M_r = 567.20$

Monoclinic, $P2_1/c$

Hall symbol: -p 2ybc

$a = 11.8862 (18) \text{ \AA}$

$b = 5.6431 (9) \text{ \AA}$

$c = 15.500 (2) \text{ \AA}$

$\beta = 95.687 (2)^\circ$

$V = 1034.5 (3) \text{ \AA}^3$

$Z = 2$

$F(000) = 580$

$D_x = 1.821 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1733 reflections

$\theta = 2.6\text{--}24.8^\circ$

$\mu = 1.20 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Needle, pale green

$0.15 \times 0.13 \times 0.07 \text{ mm}$

Data collection

Siemens SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scan

7195 measured reflections

1822 independent reflections

1488 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 2.6^\circ$

$h = -14 \rightarrow 13$

$k = -6 \rightarrow 6$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.068$

$S = 1.03$

1822 reflections

166 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.8247P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.0000	0.5000	0.01764 (14)
S1	0.22867 (5)	0.52524 (11)	0.32025 (4)	0.02534 (17)
O1	0.03642 (14)	0.3493 (3)	0.36616 (11)	0.0251 (4)
N1	-0.33708 (16)	0.0597 (4)	0.46039 (13)	0.0214 (5)
C1	-0.3094 (2)	0.2565 (5)	0.41861 (17)	0.0267 (6)

H1	-0.3640	0.3791	0.4099	0.032*
O2	0.42671 (14)	0.2203 (3)	0.40344 (10)	0.0223 (4)
N2	0.04253 (19)	-0.0307 (4)	0.33372 (17)	0.0349 (6)
C2	-0.2055 (2)	0.2898 (5)	0.38770 (18)	0.0285 (6)
H2	-0.1895	0.4322	0.3586	0.034*
O3	0.41911 (15)	-0.0211 (3)	0.28832 (12)	0.0307 (4)
N3	0.14163 (18)	0.0782 (4)	0.30919 (16)	0.0329 (6)
C3	-0.1253 (2)	0.1121 (5)	0.39981 (16)	0.0227 (6)
O4	0.49432 (15)	-0.2945 (3)	0.41919 (12)	0.0258 (4)
C4	-0.1526 (2)	-0.0926 (5)	0.44222 (16)	0.0254 (6)
H4	-0.0996	-0.2183	0.4512	0.030*
C5	-0.2588 (2)	-0.1107 (5)	0.47130 (16)	0.0229 (6)
H5	-0.2769	-0.2515	0.5005	0.027*
C6	-0.0151 (2)	0.1322 (5)	0.36561 (17)	0.0241 (6)
C7	0.13385 (19)	0.2981 (5)	0.32989 (16)	0.0233 (6)
C8	0.3334 (2)	0.3561 (5)	0.26933 (16)	0.0241 (6)
H8A	0.2953	0.2784	0.2171	0.029*
H8B	0.3895	0.4684	0.2495	0.029*
C9	0.39724 (19)	0.1663 (5)	0.32486 (16)	0.0210 (5)
H4B	0.459 (2)	-0.417 (3)	0.4250 (18)	0.032*
H4A	0.470 (2)	-0.229 (5)	0.3738 (11)	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0149 (2)	0.0173 (2)	0.0210 (2)	0.00045 (18)	0.00284 (17)	0.00042 (19)
S1	0.0185 (3)	0.0219 (3)	0.0362 (4)	0.0001 (3)	0.0056 (3)	0.0036 (3)
O1	0.0187 (9)	0.0241 (10)	0.0338 (10)	0.0013 (8)	0.0087 (8)	-0.0002 (8)
N1	0.0174 (11)	0.0225 (11)	0.0245 (11)	-0.0009 (9)	0.0030 (9)	-0.0010 (9)
C1	0.0225 (14)	0.0194 (13)	0.0393 (16)	0.0029 (11)	0.0090 (12)	0.0014 (12)
O2	0.0231 (9)	0.0221 (9)	0.0215 (10)	0.0018 (7)	0.0011 (7)	0.0020 (7)
N2	0.0254 (12)	0.0278 (13)	0.0546 (16)	-0.0049 (11)	0.0187 (11)	-0.0056 (12)
C2	0.0277 (14)	0.0201 (14)	0.0388 (16)	-0.0006 (11)	0.0095 (12)	0.0058 (12)
O3	0.0350 (11)	0.0293 (11)	0.0281 (10)	0.0086 (9)	0.0040 (8)	-0.0047 (9)
N3	0.0207 (12)	0.0244 (13)	0.0563 (16)	-0.0032 (10)	0.0178 (11)	-0.0030 (11)
C3	0.0178 (12)	0.0250 (14)	0.0253 (14)	-0.0019 (11)	0.0016 (10)	-0.0022 (11)
O4	0.0288 (11)	0.0211 (10)	0.0271 (10)	-0.0007 (8)	0.0013 (8)	0.0001 (8)
C4	0.0212 (13)	0.0262 (14)	0.0284 (14)	0.0043 (11)	0.0006 (11)	0.0016 (12)
C5	0.0213 (13)	0.0242 (14)	0.0236 (14)	0.0002 (11)	0.0038 (11)	0.0027 (11)
C6	0.0178 (13)	0.0255 (14)	0.0293 (14)	-0.0020 (11)	0.0038 (11)	0.0020 (12)
C7	0.0144 (12)	0.0266 (15)	0.0291 (14)	0.0027 (11)	0.0036 (11)	0.0026 (12)
C8	0.0164 (13)	0.0307 (15)	0.0258 (14)	0.0006 (11)	0.0049 (11)	0.0050 (12)
C9	0.0121 (12)	0.0275 (14)	0.0244 (14)	-0.0027 (11)	0.0063 (10)	0.0033 (12)

Geometric parameters (\AA , ^\circ)

Ni1—O2 ⁱ	2.0702 (16)	N2—C6	1.275 (3)
Ni1—O2	2.0702 (16)	N2—N3	1.414 (3)
Ni1—O4	2.0781 (18)	C2—C3	1.384 (3)
Ni1—O4 ⁱ	2.0781 (18)	C2—H2	0.9500

Ni1—N1 ⁱⁱ	2.1157 (19)	O3—C9	1.239 (3)
Ni1—N1 ⁱⁱⁱ	2.1157 (19)	N3—C7	1.287 (3)
S1—C7	1.723 (3)	C3—C4	1.383 (4)
S1—C8	1.811 (2)	C3—C6	1.465 (3)
O1—C7	1.367 (3)	O4—H4B	0.816 (10)
O1—C6	1.369 (3)	O4—H4A	0.819 (10)
N1—C5	1.337 (3)	C4—C5	1.385 (3)
N1—C1	1.343 (3)	C4—H4	0.9500
N1—Ni1 ^{iv}	2.1157 (19)	C5—H5	0.9500
C1—C2	1.380 (4)	C8—C9	1.528 (3)
C1—H1	0.9500	C8—H8A	0.9900
O2—C9	1.271 (3)	C8—H8B	0.9900
O2 ⁱ —Ni1—O2	180.00 (6)	C7—N3—N2	105.6 (2)
O2 ⁱ —Ni1—O4	86.66 (7)	C4—C3—C2	118.6 (2)
O2—Ni1—O4	93.34 (7)	C4—C3—C6	119.8 (2)
O2 ⁱ —Ni1—O4 ⁱ	93.34 (7)	C2—C3—C6	121.6 (2)
O2—Ni1—O4 ⁱ	86.66 (7)	Ni1—O4—H4B	127 (2)
O4—Ni1—O4 ⁱ	180.0	Ni1—O4—H4A	98 (2)
O2 ⁱ —Ni1—N1 ⁱⁱ	88.50 (7)	H4B—O4—H4A	110 (3)
O2—Ni1—N1 ⁱⁱ	91.50 (7)	C3—C4—C5	118.7 (2)
O4—Ni1—N1 ⁱⁱ	85.90 (7)	C3—C4—H4	120.6
O4 ⁱ —Ni1—N1 ⁱⁱ	94.10 (7)	C5—C4—H4	120.6
O2 ⁱ —Ni1—N1 ⁱⁱⁱ	91.50 (7)	N1—C5—C4	123.4 (2)
O2—Ni1—N1 ⁱⁱⁱ	88.50 (7)	N1—C5—H5	118.3
O4—Ni1—N1 ⁱⁱⁱ	94.10 (7)	C4—C5—H5	118.3
O4 ⁱ —Ni1—N1 ⁱⁱⁱ	85.90 (7)	N2—C6—O1	113.0 (2)
N1 ⁱⁱ —Ni1—N1 ⁱⁱⁱ	180.0	N2—C6—C3	128.2 (2)
C7—S1—C8	97.45 (12)	O1—C6—C3	118.9 (2)
C7—O1—C6	101.82 (19)	N3—C7—O1	113.0 (2)
C5—N1—C1	117.0 (2)	N3—C7—S1	129.2 (2)
C5—N1—Ni1 ^{iv}	119.62 (16)	O1—C7—S1	117.79 (18)
C1—N1—Ni1 ^{iv}	123.17 (17)	C9—C8—S1	116.64 (17)
N1—C1—C2	123.4 (2)	C9—C8—H8A	108.1
N1—C1—H1	118.3	S1—C8—H8A	108.1
C2—C1—H1	118.3	C9—C8—H8B	108.1
C9—O2—Ni1	127.26 (16)	S1—C8—H8B	108.1
C6—N2—N3	106.5 (2)	H8A—C8—H8B	107.3
C1—C2—C3	118.8 (2)	O3—C9—O2	126.3 (2)
C1—C2—H2	120.6	O3—C9—C8	117.1 (2)
C3—C2—H2	120.6	O2—C9—C8	116.5 (2)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x+1, y, z$; (iii) $-x, -y, -z+1$; (iv) $x-1, y, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
O4—H4A \cdots O3	0.82 (1)	1.83 (1)	2.633 (3)	167 (3)
O4—H4B \cdots O2 ^v	0.82 (1)	2.11 (2)	2.857 (3)	153 (3)

supplementary materials

Symmetry code: (v) $x, y-1, z$.